Table II. Preparation, Melting Points, and Ionization Constants of Mandelic Acid and Derivatives at 25 °C

acid (0.010 M)	melting point, °C lit.	exptl[a]	pK_a^T	source of data[b]
2,4-dichloromandelic	120-121	120-121	3.12 ± 0.05[c]	8
		119-121	3.29 ± 0.14	4
3,4-dichloromandelic	113-115	114-114.5	3.13 ± 0.05	6
p-chloromandelic	120-121	120-121	3.22 ± 0.06	6
m-nitromandelic	119-120	114-118	3.28 ± 0.04	4
p-bromomandelic	117-119	116-118	3.28 ± 0.02	8
p-nitromandelic	126-127	124-127	3.34 ± 0.04	4
m-hydroxymandelic	131-132	130-132	3.38 ± 0.02	8
		130-130.5	3.39 ± 0.04	6
m-chloromandelic	115-115.5	114-115.5	3.39 ± 0.02	4
mandelic	118-120	118-120	3.39 ± 0.01	8
		118-120	3.40 ± 0.01	8
		120-121	3.40 ± 0.04	6
4-hydroxy-3-methoxymandelic	132-134	133-135	3.42 ± 0.03	8
o-nitromandelic	138-140	137-141	3.44 ± 0.02	4
m-bromomandelic	113-116	109-110	3.44 ± 0.03	4
m-methylmandelic	111-112	111-112	3.45 ± 0.03	6
p-methylmandelic	145-145.5	145-146	3.46 ± 0.04	6
p-trifluoromethylmandelic	129-130	129-130.5	3.53 ± 0.09	4
2,4,6-trimethylmandelic	132-134	133-135	3.61 ± 0.05	6
p-phenylmandelic	201-203	194-198	3.79 ± 0.04	8

[a] As determined with the Fisher-Johns melting point apparatus. Thermometer calibrated against standards of known melting point. [b] Preparation or procurement of these acids described in the theses indicated. References to original literature sources are also given. [c] Obtained by taking antilogarithms of each pK_a value in the set of results, averaging these, and writing down the logarithm of the average as pK_a. The largest deviation between this value and any value in the set is written after the pK_a as its scatter (*1*).

where I, the ionic strength, is equal to $0.5 \sum cz^2$ with c equal to the molar concentration of the ions involved and z equal to their valency. The thermodynamic constant can be estimated from the equation $pK_a^T = pK_a^M \pm 0.5(I_m^{1/2})$ where I_m is the ionic strength at the mid-point in the titration. Since $I_m \simeq 0.005$ for a 0.01 M titration as used in this work the values of pK_a^M and pK_a^T differ by about 0.035 pK units. The results are tabulated in Table II.

Literature Cited

(1) Albert, A. A., Serjeant, E. P., "Ionization Constants of Acids and Bases", Wiley, New York, N.Y., 1962.

(2) Alimarin, I. P., Shen, H.-H., *Vestn. Mosk. Univ., Khim.*, **15**, (6), 39-41 (1960).

(3) Grimsell, E., *Ark. Kemi, Mineral. Geol.*, **15** (17), 1-10 (1942).

(4) Harrington, A. E., M.S. Thesis, Xavier University, Cincinnati, Ohio, 1974.

(5) Klingenberg, J. J., Thole, J. P., Lingg, J. D., *J. Chem. Eng. Data*, **11**, 94 (1966).

(6) Knecht, D. S., M.S. Thesis, Xavier University, Cincinnati, Ohio, 1968.

(7) Kortum, G., Vogel, W., Andrussow, K., "Dissociation Constants of Organic Acids in Aqueous Solution", Butterworths, London, 1961.

(8) Meyer, R. L., M.S. Thesis, Xavier University, Cincinnati, Ohio, 1977.

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Effect of Pressure on the Viscosity of Aqueous NaCl Solutions in the Temperature Range 20–150 °C

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The paper presents a detailed study of the effect of pressure on the viscosity of aqueous NaCl solutions in the range 20–150 °C and the concentration range 0–5.4 *m*. The viscosity was measured by the oscillating-disk method in the pressure range 0–30 MPa at six concentrations along a large number of isotherms. The experimental results have an estimated uncertainty of ±0.5%. The results constitute the first measurements of the viscosity of NaCl solutions over an extended range of pressure, temperature, and concentration. The experimental data have been correlated in terms of pressure, temperature, and concentration. The correlation reproduces the original data to within the quoted uncertainty. The paper includes comparisons between the correlation and the experimental results of other investigators.

1. Introduction

It is now recognized that a knowledge of the viscosity of concentrated aqueous salt solutions is required for a number of geophysical and engineering applications. For example, the measurement of the permeability of porous media requires this knowledge for its evaluation. Similar data are needed for the calculation of the motion of geothermal fluids through wells and ducts, for the modeling of geothermal reservoirs, and for the design of extraction and power generation equipment for the utilization of geothermal energy.

On the other hand, a review of available literature (*2*, *17*) shows that measurements of the pressure effect are nonexistent for any solutions, except for our earlier work on NaCl (*7*). At atmospheric pressure there exist abundant data for NaCl and KCl solutions (*2*, *17*) which, however, do not reach beyond a

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Table I. Characteristics of the Oscillating-Disk Viscometer

radius of disk, R	33.97_3 mm
thickness of disk, d	3.21_3 mm
moment of inertia of disk, I	5477_5 g mm^2
separation between disk and fixed plates, b	2.97_8 mm
period of oscillation in air at 25 °C, T_0	16.404 s
decrement in vacuo at 25 °C, Δ_0	0.3×10^{-4}

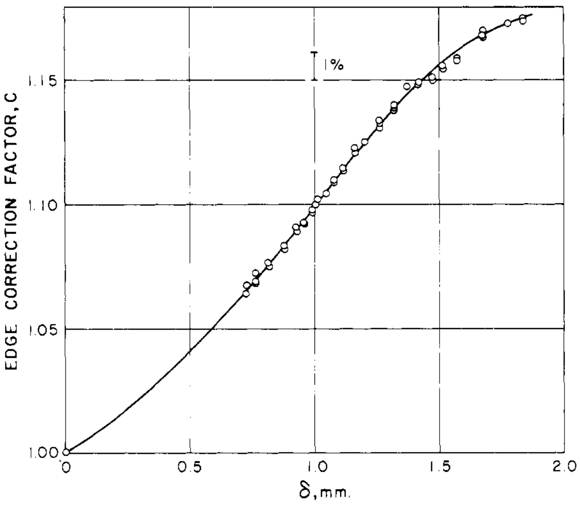

Figure 1. The calibration curve of the viscometer.

temperature of 150 °C or, often, a limited concentration range.

The present paper is the second in a series whose goal it is to create a basis for the eventual calculation of the viscosity of more complex ionic solutions. The approach is to begin with a rather thorough coverage of the viscosity of single-salt solutions. Here we treat NaCl solutions and cover the range of pressures from 0.1 to 30 MPa, the temperature range from 20 to 150 °C, and the complete concentration range. Measurements have been made with the aid of our intermediate-temperature oscillating-disk viscometer and with an estimated accuracy of ±0.5%. The preceding three ranges have been covered rather densely (nominal 3–4 MPa intervals, 5–25 °C intervals, and 1 *m* intervals) and a careful correlation, suitable for computer use, is also provided.

2. Experimental Procedure

The viscosity was measured by means of an oscillating-disk viscometer operating in the relative mode. The instrument has been described in detail (*8*). The viscometer was calibrated with respect to distilled water. The reference values of the viscosity of water needed for the calibration were taken from the accurate correlation of ref 10. Table I contains the important characteristics of the suspension system, and Figure 1 shows the calibration curve. The latter is accurately represented by the expression

$$C(\delta) = 1.0000 + 0.02881(\delta/\text{mm}) + 0.1126(\delta/\text{mm})^2 - 0.04134(\delta/\text{mm})^3 \quad (1)$$

in which $C(\delta)$ is the edge-correction factor (*9*, *11*) and δ is a measure of the boundary layer thickness:

$$\delta = (T_0\nu/2\pi)^{1/2} \quad (2)$$

where T_0 is the period of oscillation in vacuo. The maximum deviation of the calibration points from the correlation of eq 1 is less than 0.3%, while the standard deviation is one of 0.1%. The viscometer was dismantled, cleaned, and realigned after each filling and heating cycle. The calibration was checked after each such maintenance operation. On the basis of these check-measurements we assess the reproducibility of the calibration as ±0.3%.

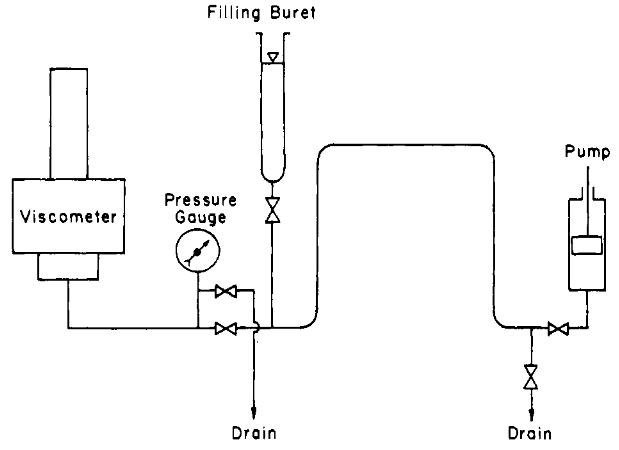

Figure 2. The filling and pressurizing system.

The NaCl solutions were prepared gravimetrically by means of a precision, high-capacity balance. Triple-distilled, deaerated water was mixed with reagent purity salt. After preparing each solution, the density of a sample was determined at room temperature using a precision pycnometer.

The measuring technique is identical with that employed for water and described elsewhere (*6*, *8*). However, a modification of the pressurizing procedure was necessary in order to avoid diluting the solution inside the viscometer vessel with the distilled water displaced by the pressure pump. The feed and pressurizing circuit is shown schematically in Figure 2. A large loop of high-pressure tubing is inserted between the pump and the viscometer. The distilled water displaced by the pump into this long tube during the pressurizing process is flushed out using a fresh charge of the solution flowing under gravity from a buret. This process is repeated frequently during a pressure cycle so as to confine the distilled water to a short length of tubing on the pump side. This simple procedure proved very effective as evidenced by the measurement of the density of samples taken from the viscometer after a complete heating cycle involving as many as 12 full-pressure cycles (up to 30 MPa). Typically, a heating cycle consisted of increasing the temperature in 7–11 steps from room temperature to 150 °C and of subsequent cooling down to room temperature in 3–4 steps. Along every isotherm, the viscosity of the solution was measured over the whole pressure range in steps of about 3–4 MPa with two or three check-measurements taken on decompression. Additional checkpoints were measured during the cooling process at low pressure. After each run, the viscometer was dismantled, cleaned, realigned, reassembled, and filled with distilled water for a calibration check as already mentioned. During the maintenance process, the internal surfaces of the viscometer were visually inspected for corrosion. No signs of corrosion pitting could be seen although a slight discoloration of the concentrated solutions was noticed. The effect of these corrosion products on the density of even the most concentrated solutions was negligibly small as evidenced by the excellent agreement between the measured values of the density before and after a complete heating cycle the duration of which is nearly 2 weeks.

3. Density

As mentioned in the previous section, the density of a sample of the fresh solutions was measured in a precision pycnometer. Furthermore, after the viscosity of each solution had been measured over the whole temperature and pressure range, the density of a sample taken from the viscometer was measured again and compared with the value obtained before filling the viscometer. The purpose of these density measurements was twofold: to check the molal concentration computed from the

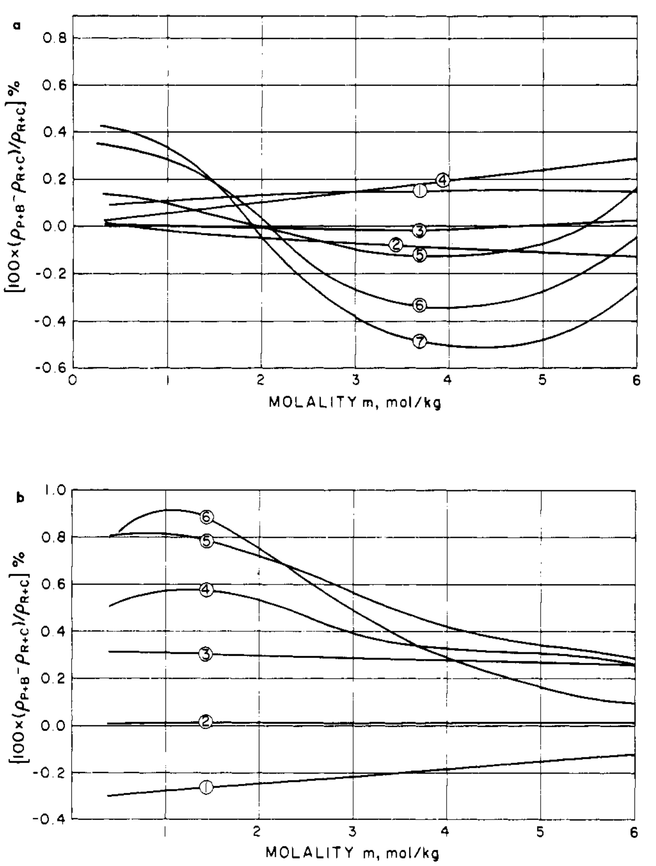

Figure 3. Comparison of the density values given in ref 16 to the correlation of ref 18: (a) at ambient pressure, 1, 0 °C; 2, 25.0 °C; 3, 50 °C; 4, 75 °C; 5, 100 °C; 6, 125 °C; 7, 150 °C; (b) at 30 MPa, 1, 25 °C; 2, 50 °C; 3, 75 °C; 4, 100 °C; 5, 125 °C; 6, 150 °C.

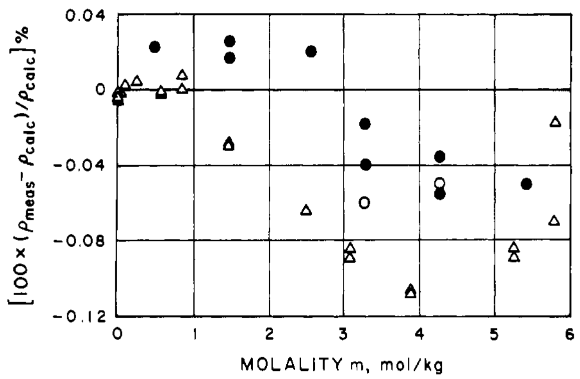

Figure 4. Comparison of the measured density at room temperature and atmospheric pressure to the correlation of ref 18: ●, present work before viscosity measurements; O, present work after viscosity measurements; Δ, data from ref 3.

Table II. Concentration and Density of the Solutions

solution no.	molality, mol/kg of H_2O	temp, °C	density,[a] kg/m^3
1	0.4755	20.9	1017.4
2	1.4713	21.0	1055.3
3	2.5514	21.6	1093.2
4	3.2672	21.2	1116.6
5	4.4289	20.8	1152.1
6	5.4054	24.2	1178.8

[a] Measured at atmospheric pressure.

gravimetric measurements and to determine whether the concentration of the brine had changed as a result of interaction with the viscometer vessel and its internal parts or as a result of the diffusion of the distilled water of the pressure pump into the viscometer.

In addition to the preceding data, the density of the individual solutions at any given pressure and temperature was needed for the evaluation of the results. The working equations of the oscillating-disk viscometer (*9*, *11*) indicate that in the first approximation

$$\Delta \sim (\mu \rho)^{1/2} \tag{3}$$

in which Δ is the measured logarithmic decrement of oscillation. The above equation indicates that the error in density affects viscosity to the same extent. An accurate determination of the density is, therefore, an essential requirement for the accurate determination of the viscosity. Although abundant data are available on the density of NaCl solutions at ambient pressure (*17*), data at high pressure are noticeably lacking. Haas (*4*) published an extensive compilation and correlation of the density of vapor-saturated NaCl solutions. The density of NaCl solutions over a wide range of temperature, pressure, and concentration has been critically evaluated, smoothed, and tabulated by Potter and Brown (*16*). The work of Rowe and Chou (*18*), although limited in temperature to 175 °C and in pressure to 35 MPa, deserves special attention since it provides a simple P, ρ, T, c equation. Figure 3a,b contains a comparison between the equation of Rowe and Chou and the smoothed values reported by Potter and Brown at saturation pressures, Figure 3a, and at 30 MPa, Figure 3b. The equation of Rowe and Chou is claimed to be accurate to within ±0.15% whereas the tabulated values of Potter and Brown have a stated uncertainty of about ±0.5% or more at temperatures higher than about 75 °C. On the basis of these comparisons we can see that the two determinations agree to within their mutual uncertainty. We have, therefore, decided to use the correlation of Rowe and Chou (*18*) in view of its simplicity and adaptability to automatic calculations.

The checkpoints measured at atmospheric pressure and room temperature in our laboratory were compared with the correlation of Rowe and Chou. Figure 4 depicts the differences between the two determinations as well as the differences between the same correlation and the direct measurements reported by Goncalves and Kestin (*3*). The maximum difference between our measurements and the correlation is only 0.06% which is within the uncertainty of the correlation. The results of ref 3 differ by no more than 0.11% from the correlation which is again within the uncertainty of the correlation.

The checkpoints obtained after the viscosity measurements were compared with the values obtained before filling the viscometer. In no case did the difference between the two values exceed the uncertainty in the density itself. This suggests the absence of a significant alteration in the composition of the solution. Table II lists the composition and density of the various solutions at atmospheric pressure and room temperature.

4. Experimental Results

The experimental results are presented in Tables III–VIII. All data have been corrected to nominal temperatures by means of a piece-wise Arrhenius expression of the form

$$\mu = A_i \exp[B_i/T] \qquad i = 1,3 \tag{4}$$

with the coefficients A_i and B_i chosen so as to give the best representation over a limited temperature range. Each entry in the tables is the average of at least two measurements performed at the same temperature and pressure. The experimental data are also shown graphically in Figures 5–10, which are included in the microfilm edition of this paper. An assessment of the accuracy of our measurements was given in ref 8. On the basis of this assessment we estimated the uncertainty in our data to range from ±0.3% below 40 °C to ±0.5% at 150 °C. However, the addition of concentration and

Table III. Viscosity of NaCl Solution No. 1 $c = 0.4755$ *m*

at 18.0 °C		at 23.5 °C		at 28.0 °C		at 40.5 °C		at 54.0 °C		at 69.0 °C	
P, MPa	μ, μPa s	*P*, MPa	μ, μPa s	*P*, MPa	μ, μPa s	*P*, MPa	μ, μPa s	*P*, MPa	μ, μPa s	*P*, MPa	μ, μPa s
0.10	1089	0.10	958	0.10	868	0.10	679	0.10	548	0.10	430
3.62	1087	3.46	957	3.58	871	3.57	679	3.57	549	3.62	434
7.07	1086	7.03	959	7.10	870	7.08	679	7.01	544	7.10	432
10.48	1087	10.34	959	10.55	868	10.51	680	10.46	543	10.48	433
13.99	1084	13.98	957	14.06	868	14.06	679	14.10	542	13.98	436
17.51	1083	17.42	957	17.51	868	17.34	681	17.48	544	17.51	439
20.61	1081	20.46	956	20.99	869	20.72	681	20.79	542	20.79	434
23.99	1084	24.03	956	24.41	868	24.23	686	24.13	544	24.10	439
26.44	1085	27.44	956	27.54	870	27.61	680	27.51	547	27.32	438
30.27	1082	30.75	956	31.16	868	31.13	683	31.04	549	30.97	441
15.79	1084	15.72	957	15.72	869	15.79	682	15.89	543	15.27	436
0.10	1090	0.10	960	0.10	868	0.10	679			0.10	429

at 84.0 °C		at 96.0 °C		at 108.5 °C		at 126.0 °C		at 148.0 °C	
P, MPa	μ, μPa s	*P*, MPa	μ, μPa s	*P*, MPa	μ, μPa s	*P*, MPa	μ, μPa s	*P*, MPa	μ, μPa s
0.10	356	0.72	311	1.07	274	0.93	234	1.00	198
3.69	358	3.38	312	3.65	275	3.51	234	5.10	201
10.55	359	10.31	314	10.25	276	8.72	237	10.38	200
17.41	360	17.34	315	23.75	280	13.55	237	15.34	202
24.01	363	24.06	317	30.70	282	18.51	238	20.65	203
30.89	365	30.54	318	16.20	278	25.20	241	25.16	204
16.13	362	7.76	314	1.41	274	30.96	242	30.51	205
0.10	356					16.51	238		
						1.55	234		

Table IV. Viscosity of NaCl Solution No. 2 $c = 1.4713$ *m*

at 19.0 °C		at 25.0 °C		at 30.0 °C		at 40.5 °C		at 54.0 °C		at 70.0 °C	
P, MPa	μ, μPa s	*P*, MPa	μ, μPa s	*P*, MPa	μ, μPa s	*P*, MPa	μ, μPa s	*P*, MPa	μ, μPa s	*P*, MPa	μ, μPa s
3.55	1164	0.10	1024	0.10	918	0.10	751	0.10	598	1.62	478
6.65	1167	3.50	1019	3.48	919	3.48	753	3.48	601	3.62	477
10.44	1168	6.98	1019	7.00	919	7.00	753	7.00	600	7.00	480
13.89	1166	10.44	1021	10.44	920	10.44	753	10.44	601	10.38	479
17.48	1166	13.89	1019	13.89	919	13.86	755	13.93	600	13.14	480
20.79	1165	17.34	1022	17.34	923	17.34	755	17.41	604	17.48	479
24.14	1166	20.79	1021	20.51	923	20.72	757	20.77	605	20.77	481
27.23	1165	24.16	1023	23.89	926	24.16	757	24.32	605	24.20	485
30.96	1166	27.68	1023	27.30	924	27.65	758	27.61	607	27.59	484
15.68	1166	31.16	1026	30.71	925	31.06	760	31.13	607	31.06	484
0.10	1166	15.68	1021	15.68	921	15.72	754	15.84	603	15.65	480
0.10	1161	0.10	1020	0.10	920	0.10	750	0.10	600	1.76	476
3.55	1160					0.10	748				

at 78.5 °C		at 98.5 °C		at 120.0 °C		at 135.5 °C		at 152.0 °C	
P, MPa	μ, μPa s	*P*, MPa	μ, μPa s	*P*, MPa	μ, μPa s	*P*, MPa	μ, μPa s	*P*, MPa	μ, μPa s
0.10	425	0.45	340	0.83	278	0.84	246	0.84	218
3.55	427	3.45	341	3.58	278	3.41	245	3.58	219
7.00	427	6.79	341	6.88	279	7.03	246	7.07	219
10.46	429	10.38	343	10.44	279	10.58	247	10.81	220
13.96	429	14.03	344	13.82	281	13.89	248	14.06	221
17.34	431	17.55	344	17.44	282	17.41	249	17.23	222
20.79	433	20.68	346	20.75	283	20.75	251	21.13	223
24.22	433	24.29	346	24.16	284	24.23	251	24.32	223
27.56	433	27.68	348	27.41	285	27.78	252	27.61	225
31.13	436	31.09	348	31.16	286	31.16	252	31.16	225
15.62	431	18.51	345	15.30	282	16.03	249	15.94	222
0.10	426	1.22	340	0.83	277	1.17	245	2.02	219
0.10	428								

the associated uncertainty in density make it necessary to estimate the uncertainty in the present data as ±0.5% over the whole temperature, pressure, and concentration range.

5. Analysis and Correlation of Results

An examination of Figures 5–10 reveals that the viscosity varies only weakly with pressure; the variation being of the order 1% over a pressure range from atmospheric to about 30 MPa. It is, therefore, sufficient to account for the pressure effect by a linear factor.

$$\mu(P,T,c) = \mu^0(T,c)[1 + \beta(T,c)P] \qquad (5)$$

The zero-pressure viscosity μ^0 and the pressure coefficient β were extracted from the experimental results by least-squares fitting. The straight lines represented by eq 5 are shown in Figures 5–10.

(*a*) *The Pressure Coefficient*. The variation of the viscosity with pressure is of a similar order of magnitude to the uncertainty in the experimental values (1–2% vs. 0.5%). This means that the experimental uncertainty will be reflected as a relatively large uncertainty in the pressure coefficient, β, defined in eq 5. We estimate the uncertainty in β to be of the order of ±20%. This made it impractical to correlate the pressure coefficients directly. For this reason we provided a correlation that preserves the recognizable trends in the dependence of β on T and c, instead of aiming for a direct correlation of these coefficients. In order

Table V. Viscosity of NaCl Solution No. 3 $c = 2.5514\ m$

at 19.0 °C		at 25.0 °C		at 30.5 °C		at 41.0 °C		at 60.0 °C		at 80.0 °C	
P, MPa	μ, μPa s	P, MPa	μ, μPa s	P, MPa	μ, μPa s	P, MPa	μ, μPa s	P, MPa	μ, μPa s	P, MPa	μ, μPa s
0.10	1289	0.10	1132	0.10	1016	0.10	834	0.21	618	0.17	474
3.65	1293	3.65	1136	3.69	1017	3.62	835	3.72	619	3.62	476
7.41	1293	7.13	1138	7.20	1019	7.10	836	7.07	621	7.13	477
10.72	1293	10.72	1137	10.65	1022	10.58	839	10.44	620	10.55	479
14.34	1293	14.17	1142	14.10	1023	14.27	840	14.17	622	14.10	479
17.54	1295	17.51	1143	17.51	1023	17.27	843	17.44	623	17.34	481
20.65	1302	20.85	1147	20.85	1026	20.92	848	20.60	624	20.65	482
23.34	1298	24.23	1149	23.96	1026	24.06	845	23.96	626	23.96	483
27.06	1299	27.68	1151	27.61	1029	26.71	844	27.61	631	27.47	484
30.28	1304	31.06	1147	31.13	1030	30.85	847	30.92	631	30.78	486
				15.82	1024	15.75	840	0.14	616	0.17	474
				0.10	1019	0.10	834				

at 101.0 °C		at 121.0 °C		at 136.0 °C		at 151.0 °C	
P, MPa	μ, μPa s	P, MPa	μ, μPa s	P, MPa	μ, μPa s	P, MPa	μ, μPa s
0.58	378	0.65	314	0.72	278	0.79	249
3.51	378	3.62	315	3.55	278	3.58	250
7.13	379	6.89	315	6.86	279	5.96	251
10.58	381	10.38	315	10.17	281	10.41	251
13.99	382	13.96	317	13.96	281	13.82	253
17.44	382	17.27	319	17.51	283	17.48	254
20.68	385	20.54	320	20.61	283	20.61	255
23.82	385	23.82	321	24.06	284	23.99	255
27.27	386	27.27	322	27.27	285	27.13	256
30.85	386	30.65	323	30.75	286	30.58	257
16.10	382	1.07	313	1.45	278	1.93	249
0.65	377						

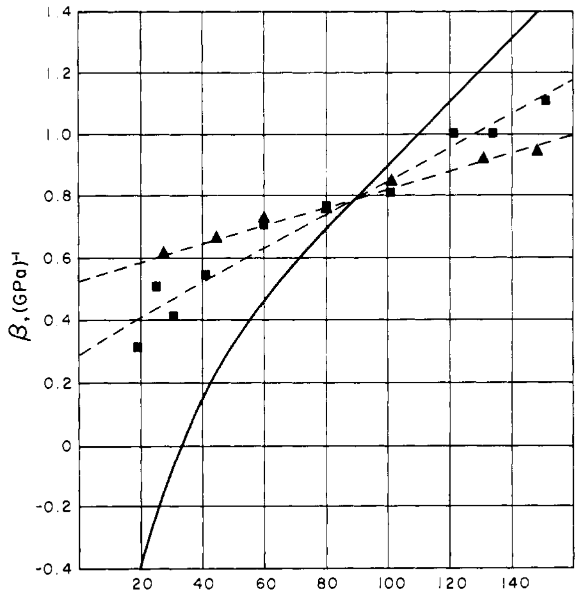

Figure 11. The pressure coefficient β: ■, solution 3; ▲, solution 6; —, distilled water (8).

to retrieve the pressure coefficient of pure water at the limit of zero concentration, the correlation was developed for the excess pressure coefficient

$$\beta^E(T,c) = \beta(T,c) - \beta(T,0) \tag{6}$$

in which $\beta(T,0) = \beta_w(T)$ is the pressure coefficient for water given in ref 2 as

$$\beta_w(T)/[\text{GPa}]^{-1} = -1.297 + (0.574 \times 10^{-1})(T/°\text{C}) - (0.697 \times 10^{-3})(T/°\text{C})^2 + (0.447 \times 10^{-5})(T/°\text{C})^3 - (0.105 \times 10^{-7})(T/°\text{C})^4 \tag{7}$$

Figure 11 shows β as a function of T for $c = 2.5514$ and $c = 5.4054\ m$. The pressure coefficient for water is also shown

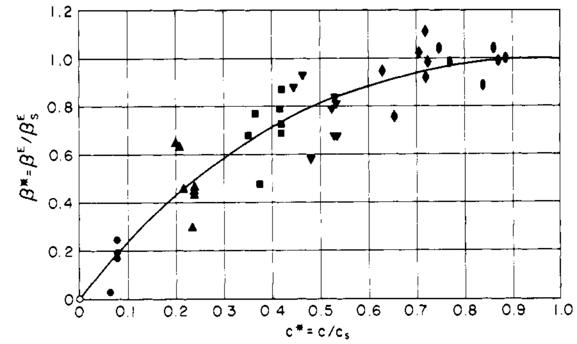

Figure 12. The reduced excess pressure coefficient β^*: ●, solution 1; ▲, solution 2; ■, solution 3; ▼, solution 4; ♦, solution 5; ▮, solution 6.

as a continuous line. We define the reduced excess pressure coefficient

$$\beta^* = \beta^E(T,c)/\beta_s^E(T) \tag{8}$$

in which β_s^E is the excess pressure coefficient at the saturation concentration, $c_s(T)$. The saturation excess pressure coefficient is adequately represented by the expression

$$\beta_s^E(T)/[\text{GPa}]^{-1} = 0.545 + (0.28 \times 10^{-2})(T/°\text{C}) - \beta_w(T) \tag{9}$$

The reduced coefficient, β^*, is represented by the following function of the reduced concentration $c^* \equiv c/c_s$:

$$\beta^*(c^*) = 2.5c^* - 2.0c^{*2} + 0.5c^{*3} \tag{10}$$

Here the concentration at saturation was taken from ref 19 and is conveniently expressed by

$$c_s(T)/[m] = 6.044 + (0.28 \times 10^{-2})(T/°\text{C}) + (0.36 \times 10^{-4})(T/°\text{C})^2 \tag{11}$$

with $m = 1$ mol of NaCl/kg of H_2O. Figure 12 depicts the

Table VI. Viscosity of NaCl Solution No. 4 $c = 3.2672\ m$

at 19.5 °C		at 25.0 °C		at 31.0 °C		at 40.0 °C		at 55.0 °C		at 70.0 °C	
P, MPa	μ, μPa s	P, MPa	μ, μPa s	P, MPa	μ, μPa s	P, MPa	μ, μPa s	P, MPa	μ, μPa s	P, MPa	μ, μPa s
0.10	1401	0.10	1241	0.10	1096	0.10	926	0.10	723	0.79	584
3.55	1401	3.62	1241	3.57	1096	3.45	928	0.10	724	0.79	586
7.07	1405	7.01	1243	7.01	1097	7.00	930	0.45	723	0.90	587
10.48	1405	10.51	1242	10.48	1100	10.39	931	1.41	725	2.17	585
13.91	1407	13.96	1241	13.96	1101	13.86	931	3.29	723	2.19	587
17.34	1411	17.37	1242	17.48	1101	17.48	933	6.96	726	3.51	586
20.36	1412	20.66	1247	20.82	1107	20.92	934	10.41	728	7.04	588
24.30	1415	24.44	1248	24.26	1106	24.27	937	13.93	729	10.43	589
27.80	1417	27.72	1252	27.59	1111	27.68	936	17.34	731	13.96	590
31.25	1419	31.20	1256	31.13	1113	31.09	940	20.79	733	17.34	595
15.48	1409	17.51	1248	15.62	1102	17.17	931	24.14	732	20.82	597
0.10	1403	0.10	1241	0.10	1095	0.10	924	27.68	736	24.23	596
								31.06	739	27.68	597
								15.96	730	31.08	600
								0.10	725	15.82	591
										1.24	586

at 84.0 °C		at 98.5 °C		at 113.0 °C		at 131.5 °C		at 154.0 °C	
P, MPa	μ, μPa s	P, MPa	μ,μPa s	P, MPa	μ, μPa s	P, MPa	μ, μPa s	P, MPa	μ, μPa s
0.86	494	0.77	421	0.88	366	0.72	313	0.81	265
1.03	494	0.93	422	0.89	366	0.85	313	1.03	265
2.17	495	2.20	421	2.17	366	2.17	312	2.48	265
3.56	496	3.51	422	3.48	367	3.51	313	3.55	266
7.01	496	7.01	424	7.00	368	7.01	314	7.01	267
10.44	497	10.41	425	10.41	369	10.48	314	10.62	268
13.96	498	13.99	426	13.93	370	14.03	316	13.96	270
17.36	499	17.25	426	17.41	371	17.51	318	17.38	270
20.75	501	20.79	428	20.67	372	20.77	318	20.82	271
24.27	503	24.16	429	24.23	374	24.20	319	24.23	272
27.65	504	27.63	431	27.58	375	27.66	320	27.65	272
31.11	504	31.09	432	31.08	376	31.09	322	31.21	273
15.99	498	15.99	426	16.32	370	15.98	317	16.17	269
1.05	493	0.95	421	0.88	365	1.07	312	1.69	266

Table VII. Viscosity of NaCl Solution No. 5 $c = 4.4289\ m$

at 25.5 °C		at 35.0 °C		at 35.5 °C		at 45.0 °C		at 56.0 °C		at 71.0 °C	
P, MPa	μ,μPa s	P, MPa	μ, μPa s	P, MPa	μ, μPa s	P, MPa	μ, μPa s	P, MPa	μ, μPa s	P, MPa	μ, μPa s
0.10	1412	0.10	1166	0.10	1151	0.10	974	0.10	818	0.79	662
3.55	1413	3.53	1171	3.53	1153	3.48	973	3.63	817	3.48	662
7.03	1415	7.10	1170	7.00	1156	7.20	978	7.01	821	7.00	663
10.63	1419	10.51	1176	10.73	1157	10.51	980	10.65	819	10.46	664
14.12	1422	14.03	1179	13.96	1158	14.10	980	14.10	823	13.96	666
17.55	1423	17.48	1180	17.37	1161	17.52	983	17.48	826	17.51	670
20.82	1428	20.79	1183	20.29	1164	20.89	985	20.79	827	20.79	671
24.37	1431	24.30	1185	24.41	1168	24.20	983	24.16	828	24.34	671
27.75	1439	27.82	1191	27.73	1169	27.42	988	27.68	832	27.75	674
31.15	1437	31.09	1193	30.71	1173	31.23	988	31.06	834	31.11	676
15.62	1422	15.62	1179	15.72	1160	15.96	981	15.86	825	15.75	668
0.10	1413	0.10	1166	0.10	1151	0.10	970	0.10	814	1.27	659
0.10	1410			0.10	1152	0.10	973			0.79	663

at 85.0 °C		at 97.0 °C		at 114.0 °C		at 129.0 °C	
P, MPa	μ, μPa s	P, MPa	μ, μPa s	P, MPa	μ, μPa s	P, MPa	μ, μPa s
1.00	558	1.00	489	1.47	414	1.14	361
3.48	556	3.48	490	3.64	415	3.38	365
7.12	560	7.07	492	7.05	415	7.00	365
10.55	562	10.50	493	10.44	418	10.51	366
14.06	563	14.22	494	14.03	419	14.08	366
17.48	563	17.55	496	17.46	419	17.41	369
20.68	565	20.73	497	21.03	421	20.72	369
24.25	568	23.96	498	24.23	422	24.16	370
27.68	569	27.08	499	27.65	424	27.59	373
31.13	570	28.09	500	30.78	426	30.37	373
15.70	563	15.94	495	15.79	419	16.14	368
0.76	557	1.08	488	1.00	413	1.65	364
1.07	557						

reduced excess pressure coefficient β^* as a function of the reduced concentration, c^*, and compares it with the original data. The agreement is reasonable within the ±20% uncertainty associated with the data points.

(b) The Zero-Pressure Viscosity. The zero-pressure viscosity $\mu^0(T,c)$ extracted from the least-squares fit represented by eq 5 constitutes the major part of the viscosity $\mu(P,T,c)$. The function $\mu^0(T,c)$ can be greatly simplified in form if the relative

Table VIII. Viscosity of NaCl Solution No. 6, $c = 5.4054\ m$

at 27.5 °C		at 44.5 °C		at 60.0 °C		at 80.0 °C		at 94.0 °C		at 101.0 °C		at 131.0 °C		at 148.0 °C	
P, MPa	μ, μPa s	P, MPa	μ, μPa s	P, MPa	μ, μPa s	P, MPa	μ, μPa s	P, MPa	μ, μPa s	P, MPa	μ, μPa s	P, MPa	μ, μPa s	P, MPa	μ, μPa s
0.93	1525	0.10	1092	0.10	854	0.86	654	1.02	556	1.38	524	1.55	395	3.67	347
3.48	1526	3.50	1094	3.33	856	3.45	656	3.47	557	3.55	523	3.48	396	7.13	348
6.95	1529	7.12	1099	7.26	859	7.01	656	6.82	559	7.13	525	6.93	398	10.46	350
10.65	1534	11.03	1099	10.51	861	10.44	659	10.39	561	10.72	527	10.58	399	13.82	350
14.11	1535	14.24	1105	13.72	862	13.89	664	13.76	561	13.99	528	13.99	399	17.39	352
17.60	1540	17.65	1107	17.75	862	17.34	660	17.25	565	17.58	527	17.44	399	21.04	354
20.96	1545	20.81	1111	21.08	867	20.86	665	20.92	567	21.13	532	20.79	404	24.34	355
24.61	1546	24.39	1112	23.15	870	24.30	665	24.29	566	24.44	534	24.39	403	27.73	356
27.82	1551	27.86	1112	27.47	869	27.68	667	27.96	568	27.68	535	27.54	405	31.27	355
31.09	1552	31.30	1115	31.39	875	31.27	669	31.28	566	31.37	536	31.54	406	16.17	352
15.62	1536	17.39	1106	15.60	864	21.41	662	16.17	562	15.58	529	15.65	401	0.77	346
0.10	1525	0.10	1096	0.10	855	11.06	654	1.43	557	8.84	526	1.55	395		
						1.03	653			1.19	523				

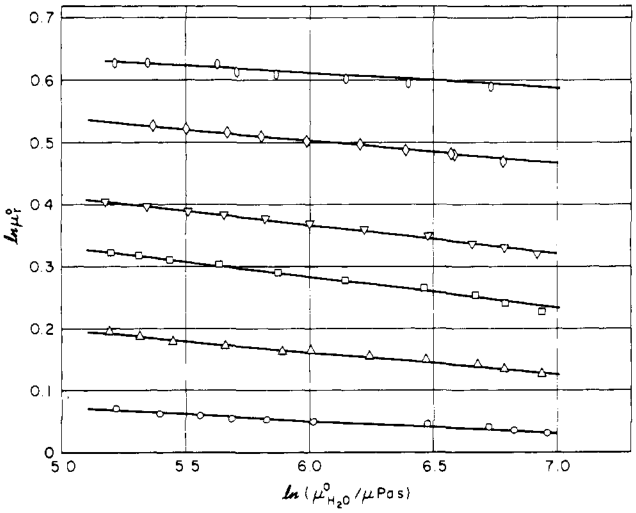

Figure 13. The relationship between ln μ_r^0 and ln $\mu_{H_2O}^0$: ○, solution 1; △, solution 2; □, solution 3; ▽, solution 4; ◇, solution 5; 0, solution 6.

viscosity $\mu_r^0(T,c)$ rather than the viscosity itself is correlated. The relative viscosity μ_r^0 is given by

$$\mu_r^0(T,c) = \mu^0(T,c)/\mu^0(T,0) \quad (12)$$

The viscosity of water at low pressure, $\mu_w^0 = \mu^0(T,0)$, was calculated from the correlation of Kestin et al. (*10*) which is reproduced here for convenience

$$\log\,[\mu_w^0(T)/\mu_w^0(20\ °\mathrm{C})] = (20 - T)[1.2378 - (1.303 \times 10^{-3}) \times (20 - T) + (3.06 \times 10^{-6})(20 - T)^2 + (2.55 \times 10^{-8}) \times (20 - T)^3]/(96 + T) \quad (13)$$

where

$$\mu_w^0(20\ °\mathrm{C}) = 1002\ \mu\mathrm{Pa\ s}$$

The correlation of μ_r^0 in terms of temperature and concentration was achieved through the application of the Othmer rule (*15*) as suggested by Korosi and Fabuss (*12*). Figure 13 shows the relationship between ln μ_r^0 and ln μ_w^0 for the various solutions. The points for any one concentration follow very closely a linear relationship, i.e.

$$\log\,[\mu_r^0(T,c)] = A(c) + B(c)\log\,[\mu_w^0(T)/\mu_w^0(20\ °\mathrm{C})] \quad (14)$$

The coefficients $A(c)$ and $B(c)$ were obtained from a least-squares fitting of the original data and correlated in terms of the molality, again by least-squares fitting. The coefficients $A(c)$ and $B(c)$ thus obtained are given by

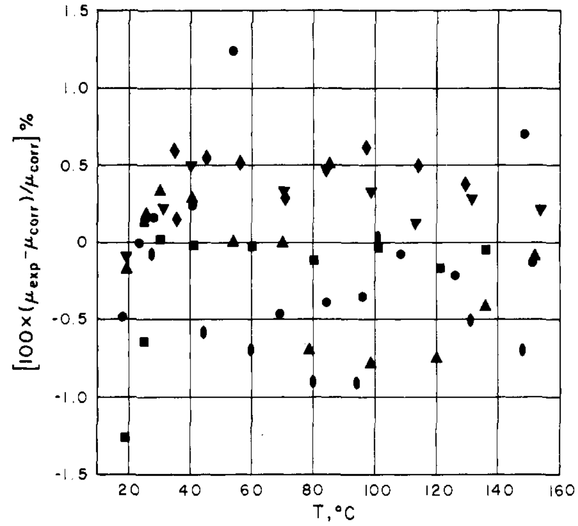

Figure 14. Comparison of the values of μ^0 to the Othmer rule (eq 14): ●, solution 1; ▲, solution 2; ■, solution 3; ▼, solution 4; ◆, solution 5; ●, solution 6.

$$A(c) = (0.3324 \times 10^{-1})(c/m) + (0.3624 \times 10^{-2})(c/m)^2 - (0.1879 \times 10^{-3})(c/m)^3 \quad (15)$$

and

$$B(c) = -(0.396 \times 10^{-1})(c/m) + (0.102 \times 10^{-1})(c/m)^2 - (0.702 \times 10^{-3})(c/m)^3 \quad (16)$$

respectively. Figure 14 is a plot of the percentage deviations of the original values of $\mu^0(T,c)$ from the ones calculated according to eq 13–16. The maximum deviation is 1.4% whereas the standard deviation is ±0.5%, which is the same as the uncertainty in the experimental results themselves.

Equation 5 supplemented by eq 6–11 for the pressure coefficient $\beta(T,c)$ and by eq 13–16 for $\mu^0(T,c)$ constitutes a complete correlation of the viscosity of NaCl solutions in terms of pressure, temperature, and concentration valid over the pressure range 0–30 MPa, the temperature range 20–150 °C, and the concentration range up to saturation. Figures 15–20, which appear only in the microfilm edition, are scatter diagrams depicting the deviations of our experimental values $\mu(P,T,c)$ from the correlation. The standard deviation of the entire set of points is ±0.5% which is of the same order of magnitude as the experimental uncertainty.

6. Comparison with Other Investigations

As mentioned earlier, experimental results on the viscosity of NaCl solutions at combined high pressures and temperatures are very scarce. We have been unable to locate any references

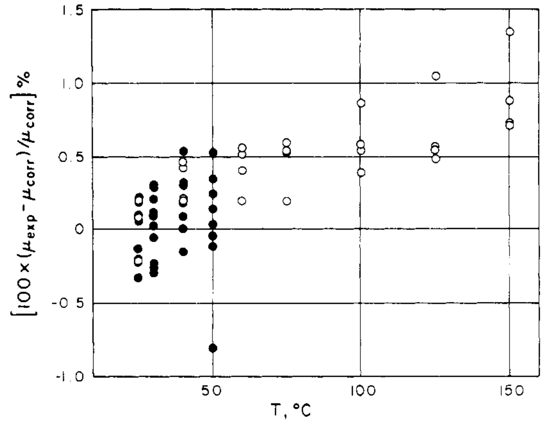

Figure 21. Comparison of the present correlation with the experimental data of ref 3 (●) and 12 (○).

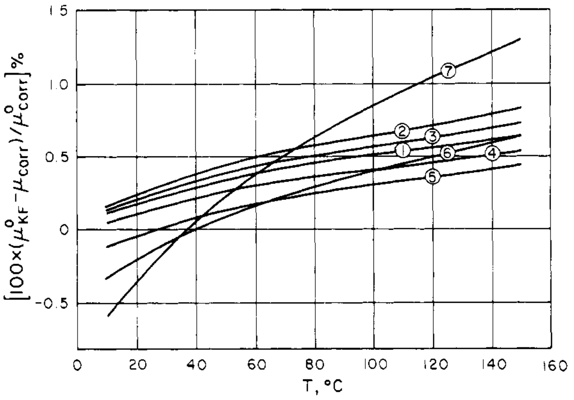

Figure 22. Comparison between the present correlation and that of ref 12: 1, 0.5 *m*; 2, 1.0 *m*; 3, 1.5 *m*; 4, 2.0 *m*; 5, 2.5 *m*; 6, 3.0 *m*; 7, 3.5 *m*.

in which experimental results at high pressure were reported. The bulk of the existing literature concerning the viscosity of NaCl solutions deals with the viscosity of dilute solutions at low temperatures and atmospheric pressure. Few investigators measured at molalities exceeding unity and still fewer measured at temperatures exceeding 70 °C. We have decided, therefore, to limit the comparison to those investigations that covered either a wide concentration range, a wide temperature range, or both. In these categories we note the work of Goncalves and Kestin (*3*), Korosi and Fabuss (*12*), Suryanarayana and Venkatesan (*20*), Lengyel et al. (*13*), Ezrokhi (*1*), Ostroff et al. (*14*), and Janz et al. (*5*). The first two investigations merit special attention: the work of Korosi and Fabuss (*12*), which is the only investigation other than the present that covers the extended temperature range 25–150 °C and the work of Goncalves and Kestin (*3*), which covers the wide molality range 0–5.8 and is closely related to the present work. Figure 21 contains the deviations of the experimental data of ref 3 and 12 from the present correlation. The standard deviation of the experimental data of Korosi and Fabuss (*12*) is ±0.6% whereas that of the data of Goncalves and Kestin (*3*) is only ±0.25%. The maximum deviation in the latter case is one of −0.8% and occurs only at one point of the 46 points taken from this reference. With the exception of this single point, the deviations remain below 0.55% which is commensurate with the accuracy claimed for the correlation (±0.5%). Figure 22 shows a comparison between the present correlation and the correlation of Korosi and Fabuss (*12*) in the temperature range 25–150 °C and the concentration range 0–3.5 *m*. We have also compared the correlation with the data given in ref 1, 5, 13, 14, and 20. The deviations are plotted as a function of concentration in Figure 23. The results of ref 20 are typically lower than the values predicted by the correlation; their standard deviation is ±0.75% with a maximum deviation of −1.6%. The 27 points reported by Lengyel et al. (*13*) agree very well with the correlation with a maximum deviation of −0.65% and a standard deviation of only ±0.2%. The standard deviation of the 15 points reported by Ezrokhi (*1*) is ±0.6% and the maximum deviation of −1.8% occurs for a solution that is nearly saturated (c = 6.15 *m*). The single-temperature measurements of Ostroff et al. (*14*) and of Janz et al. (*5*) seem in good agreement with the correlation as evident in Figure 23.

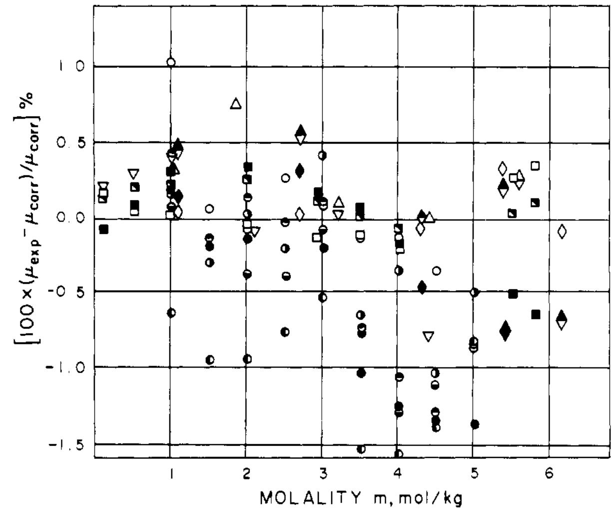

Figure 23. Comparison of the present correlation with the experimental data of ref 1, 5, 13, 14, and 20: ref 20, (○) 30 °C, (◐) 35 °C, (◑) 40 °C, (⊖) 45 °C, (◒) 50 °C, (●) 55 °C; ref 13, (□) 25 °C, (◪) 30 °C, (■) 40 °C; ref 1, (◇) 25 °C, (⬖) 40 °C, (◆) 60 °C; ref 14, (△) 25 °C; ref 5, (▽) 25 °C.

7. Summary

The measurements of the viscosity of NaCl solutions presented in this paper cover the concentration range 0–5.4 *m*, the temperature range 20–150 °C, and the pressure range 0–30 MPa. The uncertainty in these measurements is believed to be of the order of ±0.5% over the whole range of pressure, temperature, and concentration. The entire body of the experimental data has been correlated in terms of pressure, temperature, and concentration. The correlation is repeated here for convenience

$$\mu(P,T,c) = \mu^0(T,c)[1 + \beta(T,c)P] \qquad (5)$$

$$\log\,[\mu^0(T,c)/\mu_w^0(T)] = A(c) + B(c)\log\,[\mu_w^0(T)/\mu_w^0(20\ ^\circ\mathrm{C})] \qquad (14)$$

$$\log\,[\mu_w^0(T)/\mu_w^0(20)] = (20 - T)[1.2378 - (1.303 \times 10^{-3}) \times (20 - T) + (3.06 \times 10^{-6})(20 - T)^2 + (2.55 \times 10^{-8}) \times (20 - T)^3]/(96 + T)$$

with

$$\mu_w^0(20\ ^\circ\mathrm{C}) = 1002\ \mu\mathrm{Pa\ s}$$

$$A(C) = (0.3324 \times 10^{-1})(c/m) + (0.3624 \times 10^{-2})(c/m)^2 - (0.1879 \times 10^{-3})(c/m)^3 \qquad (15)$$

$$B(C) = -(0.396 \times 10^{-1})(c/m) + (0.102 \times 10^{-1})(c/m)^2 - (0.702 \times 10^{-3})(c/m)^3 \qquad (16)$$

$$\beta(T,C) = \beta_s^E(T)\beta^*(c/c_s) + \beta_w(T) \qquad (6,\ 8)$$

$$\beta_w(T)/[\mathrm{GPa}]^{-1} = -1.297 + (0.574 \times 10^{-1})(T/^\circ\mathrm{C}) - (0.697 \times 10^{-3})(T/^\circ\mathrm{C})^2 + (0.447 \times 10^{-5})(T/^\circ\mathrm{C})^3 - (0.105 \times 10^{-7})(T/^\circ\mathrm{C})^4 \qquad (7)$$

$$\beta_s^E(T)/[\mathrm{GPa}]^{-1} = 0.545 + (0.28 \times 10^{-2})(T/°\mathrm{C}) - \beta_w(T) \quad (9)$$

$$c_s(T)/[m] = 6.044 + (0.28 \times 10^{-2})(T/°\mathrm{C}) + (0.36 \times 10^{-4})(T/°\mathrm{C})^2 \quad (11)$$

$$\beta^*(c^*) = 2.5c^* - 2.0c^{*2} + 0.5c^{*3}$$

with $c^* = c/c_s$.

In the above equations all viscosities are expressed in μPa s, pressure is expressed in MPa, temperature is expressed in °C, and concentration is expressed as a molality, m = mol of NaCl/kg of H_2O. The above set of equations reproduces the original data within a standard deviation of ±0.5% which is comparable with the uncertainty in the data values themselves. A comparison with other investigations reveals that our correlation agrees with the results of Goncalves and Kestin (*3*) and those of Korosi and Fabuss (*12*) to within the combined uncertainty. The results of Suryanarayana and Venkatesan (*20*) deviate from our correlation by as much as 1.6% with a standard deviation of ±0.75%; the deviations are predominantly on the negative side. The data of Lengyel et al. (*13*) Ezrohki (*1*), Ostroff et al. (*14*), and Janz et al. (*5*) are in reasonable agreement with the present correlation.

Acknowledgment

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Literature Cited

(1) Ezrokhi, L. L., *J. Appl. Chem. USSR (Engl. Transl.)*, **25**, 917 (1952).
(2) Fair, J. A., Ozbeck, H., "Viscosity and Density Tables of Sodium Chloride Solutions (compilation)", National Geothermal Information Resource, Lawrence Berkeley Laboratory, University of California.
(3) Goncalves, F. A., Kestin, J., *Ber. Bunsenges. Phys. Chem.*, **81**, 1156 (1977).
(4) Haas, J. L., Jr., *U. S., Geol. Surv., Bull.*, **No. 1421-B** (1976). See also *Am. J. Sci.*, **269**, 490 (1970).
(5) Janz, G. J., Oliver, B. G., Lakshminarayanan, G. R., Mayer, G. E., *J. Phys. Chem.*, **74**, 1285 (1970).
(6) Kestin, J., Khalifa, H. E., *Appl. Sci. Res.*, **32**, 483 (1976).
(7) Kestin, J., Khalifa, H. E., Ro, S. T., Wakeham, W. A., *J. Chem. Eng. Data*, **22**, 207 (1977).
(8) Kestin, J., Khalifa, H. E., Sookiazian, H., Wakeham, W. A., *Ber. Bunsenges. Phys. Chem.*, **82**, 180 (1978).
(9) Kestin, J., Leidenfrost, W., Liu, C. Y., *Z. Angew. Math. Phys.*, **10**, 558 (1959).
(10) Kestin, J., Sokolov, M., Wakeham, W. A., *J. Phys. Chem. Ref. Data*, in press.
(11) Kestin, J., Wang, H. E., *J. Appl. Mech.*, **79**, 197 (1957).
(12) Korosi, A., Fabuss, B. M., *J. Chem. Eng. Data*, **13**, 548 (1968).
(13) Lengyel, S., Tamas, J., Giber, J., Holderith, J., *Magy. Kem. Foly.*, **70**, 66 (1964).
(14) Ostroff, A. G., Snowden, B. S., Woessner, O. E., *J. Phys. Chem.*, **73**, 2784 (1969).
(15) Othmer, D. G., Yu, E. S., *Ind. Eng. Chem.*, **60**, 22 (1968).
(16) Potter, R. W., II, Brown, D. L., *U. S., Geol. Surv., Bull.*, **No. 1421-C** (1977).
(17) Potter, R. W., II, Shaw, D. R., Haas, J. L., Jr., *U. S., Geol. Surv., Bull.*, **No. 1417** (1975).
(18) Rowe, A. M., Jr., Chou, J. C. S., *J. Chem. Eng. Data*, **15**, 61 (1970).
(19) Seidell, A., "Solubilities of Inorganic and Metal Organic Compounds", Vol. 1, Van Nostrand, New York, N.Y., 1940.
(20) Suryanarayana, C. V., Venkatesan, V. K., *Trans. Faraday Soc.*, **54**, 1709 (1952).

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Supplementary Material Available: Figures 5–10, which display the viscosity of the six solutions as a function of pressure along various isotherms, and Figures 14–20, which contain plots of the deviations of the present experimental results (18 pages). Ordering information is given on any current masthead page.

Liquid–Liquid Equilibria in the Reciprocal Ternary System Cs, Li ‖ Cl, F

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The miscibility gap in the molten system Cs, Li || Cl, F as a function of composition and temperature was completely measured. The upper critical solution temperature of this system was found at 912 °C and $x_{\mathrm{LiF}} = 0.540$, $x_{\mathrm{LiCl}} = 0.235$, and $x_{\mathrm{CsF}} = 0.225$ (x = mole fraction). The experimental results were compared with those calculated on the basis of the conformal ionic solution theory.

In the past few years, a serial work (*5*), meant to systematically analyze the liquid immiscibility of ionic salts at high temperatures, was carried out in our laboratory; among the mixtures formed by lithium fluoride and alkali halides, the system Cs, Li || Cl, F showed a large demixing phenomenon along the stable diagonal (LiF + CsCl) (*4*).

Solid–liquid (SL) equilibria for this system were given by Bukhalova and Sementsova (*2*); no data on the liquid–liquid (LL) equilibria were previously reported.

The present paper studies the miscibility gap in the whole composition square as a function of temperature.

Experimental Section

The apparatus employed, which allows direct observation of the sample contained in the quartz vessel, is fully described (*7*).

The materials used were CsCl, CsF, LiCl, and LiF "Merck Suprapur". Particular care was devoted to the drying of the samples to prevent loss of transparency of the vessel. Devetrification phenomena of silica caused no problems during the performance of the experiments.

Results

Table I reports the measured LL and SL equilibria temper-

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